Rheological behavior of polyamide-6 based nanocomposites: experimental study and modeling

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Rheological Behavior of Polyamide-6 Based Nanocomposites: Experimental Study and Modeling

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Abstract. Rheological behavior of polyamide-6 based nanocomposite (PNC) with 2-wt% organoclay was studied in a simple shear transient flow. The experimental data were compared with the modified Giesekus model used to study the effect of particle/polymer interactions on rheological properties. Comparison of the experimental data with the model predictions showed good qualitative agreement of transient behavior of PNC.

INTRODUCTION

The polymer nanocomposites are a class of filled materials, in which the size of nanoparticles amplifies the effect of interaction between the nanoparticles and the polymer matrix. Depending on the nanoparticle dispersion and the particle/polymer interactions, the effective volume of reinforced particles changes and affects the flow behavior of the nanocomposites as well as their performance at solid state. The rheology of nanocomposites can give valuable information about the nanoscale dispersion, interaction and structure of the materials [1, 2].

THEORETICAL

The nanoparticles we consider in the present work are disk-shaped nanoparticles with aspect ratio $r = a/b$ ($a<b$), where a and b are the thickness and the diameter of the disk, respectively. The equation of change for the second order tensor orientation tensor **a2** can be written as follows:

$$\mathbf{a2}_{(1)} = (\chi - 1)(\mathbf{d}\cdot\mathbf{a2} + \mathbf{a2}\cdot\mathbf{d}) - 2\chi\mathbf{d}:\mathbf{a4} + \mathbf{R} \tag{1}$$

where $\mathbf{a2}_{(1)}$ is the upper-convected derivative of **a2**, **a4** the fourth-order orientation tensor, $\chi = (r^2-1)/(r^2+1)$ a geometrical factor, **d** the rate of strain tensor and **R** the diffusion tensor defined as:

$$\mathbf{R} = 2D_{rB}(\mathbf{I} - m\mathbf{a2}) + 2\mathbf{D}^{\mathbf{r}} - 3(\mathbf{a2}\cdot\mathbf{D}^{\mathbf{r}} + \mathbf{D}^{\mathbf{r}}\cdot\mathbf{a2}) - 2tr(\mathbf{D}^{\mathbf{r}})\mathbf{a2} + 6\mathbf{D}^{\mathbf{r}}:\mathbf{a4} \tag{2}$$

The rotary Brownian diffusivity, D_{rB}, in Eq. (2) is defined by $D_{rB} = 3k_BT/4\eta(\dot{\gamma})b^3$, where η is the viscosity of the polymer matrix, k_B is the Boltzmann constant and T is the absolute temperature. In Eq. (2), $\mathbf{D}^{\mathbf{r}}$ is the orientational diffusivity tensor and m is the dimension of the space. In an earlier study, Folgar and Tucker suggested a simple expression where the orientational diffusivity tensor $\mathbf{D}^{\mathbf{r}}$ is assumed to be isotropic and is expressed as $\mathbf{D}^{\mathbf{r}} = C_I\dot{\gamma}\mathbf{I}$. However, the expression for the diffusivity contains an arbitrary dimensionless fitting parameter C_I that depends in general on the particle concentration, shape and aspect ratio. As pointed out by Koch [3] the diffusivity may be used inappropriately to compensate for other factors that decrease particle orientation. Since the imposed flow field and the resulting orientation distribution function are anisotropic, there is no reason to expect that an isotropic diffusivity would be able to account for hydrodynamic particle-particle interactions. Using the insight obtained in the work by Rahnama *et al.* [4], Koch [3] derived an approximate model for the orientational diffusivity tensor resulting from

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hydrodynamic interactions in an arbitrary linear flow. Let **p** be a unit vector normal to the flat surface of the test disk, the proposed model is recast in the following form:

$$\mathbf{D}^{\mathrm{r}} = \frac{nL^3}{\dot{\gamma} ln^2 r}(\lambda_1 \mathbf{Id}:< pppp >:\mathbf{d} + \lambda_2 \mathbf{d}:< pppppp >:\mathbf{d}) \tag{3}$$

where the constants λ_1=3.16x10^{-3} and λ_2=1.13x10^{-1}.

In order to predict the rheological properties of semi-dilute nanoparticles reinforced system, an expression for the stress tensor has to be specified. A general rheological constitutive equation can be represented as follows:

$$\boldsymbol{\tau}^{\mathrm{c}} = -P\mathbf{I} + 2\eta_s \mathbf{d} + \boldsymbol{\tau}^{\mathrm{NP}} + \boldsymbol{\tau}^{\mathrm{p}} \tag{4}$$

where $\boldsymbol{\tau}^{\mathrm{NP}}$ is the nanoparticle contribution to the extra stress tensor, $\boldsymbol{\tau}^{\mathrm{p}}$ the polymer contribution with nanoparticle inclusions, and $2\eta_s \mathbf{d}$ the solvent contribution. These separate stress contributions can be expressed as:

$$\boldsymbol{\tau}^{\mathrm{NP}} = 2[\eta_s + \eta(\dot{\gamma})]\phi[A\mathbf{d}:\mathbf{a4} + B(\mathbf{d}\cdot\mathbf{a2} + \mathbf{a2}\cdot\mathbf{d}) + C\mathbf{d} + FD_{rB}\mathbf{a2}] \tag{5}$$

$$\beta\sigma\boldsymbol{\tau}^{\mathrm{p}} + \beta\frac{\alpha\lambda}{\eta_0}\boldsymbol{\tau}^{\mathrm{p}}\cdot\boldsymbol{\tau}^{\mathrm{p}} + \lambda\boldsymbol{\tau}^{\mathrm{p}}_{(1)} + \frac{m\beta(1-\sigma)}{2}(\mathbf{a2}\cdot\boldsymbol{\tau}^{\mathrm{p}} + \boldsymbol{\tau}^{\mathrm{p}}\cdot\mathbf{a2}) = 2\eta_0\mathbf{d} \tag{6}$$

In Eq. 5, ϕ is the nanoparticle volume fraction, A, B, C and F are material constants. Following the approach developed by Fan [5], Eq. (6) is the modified Giesekus model, where the constants η_0, α and λ are the polymer zero-shear viscosity, mobility factor and relaxation time, respectively. The two constants β and σ, are parameters that characterize the effect of existence (particle/polymer interaction) and orientation of nanoparticles on the hydrodynamic force acting on the polymer molecules, respectively.

EXPERIMENTAL

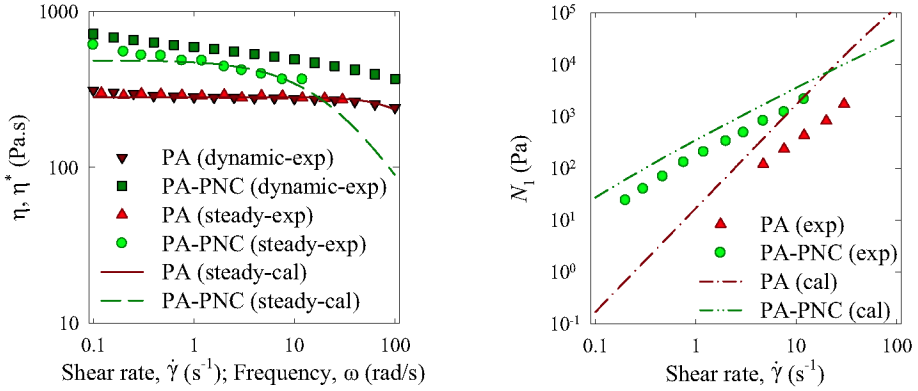
A PA-6 (PA1015B) and its commercial PNC (PA1015C2, with 2 wt% MMT-dodecylic ammonium acid, *i.e.,* 1.4 wt% inorganic clay) prepared by in-situ polymerization were purchased from Ube Industries. The molecular weight of both PA1015B and PA1015C2 is about 15 kg/mol. The XRD diffractograms and TEM observations on PA1015C2 show the fully exfoliated PNC system. The rheological measurements were carried out with strain controlled rheometer, ARES, with 25 mm parallel-plates or cone-plate geometries at T = 240°C, under a nitrogen atmosphere.

RESULTS AND DISCUSSIONS

Figure 1 shows the steady shear and linear viscoelastic dynamic results of PA1015B and PA1015C2 compared with the model predictions. The model parameters are η_0 = 283 Pa.s, α = 0.01, λ = 0.03 s, β = 1.07, σ = 1.7, C_{I} = 0.02. The steady shear data are obtained from the average of steady state values of the transient stress growth tests. The nearly constant viscosity of PA1015B, in the shear rate range of 0.1 to 100 s^{-1}, becomes shear-thinning for PA1015C2 (Fig. 1a). The complex viscosity, η^*, and steady shear viscosity, η, of PA1015B are superimposed following the Cox-Metz rule. This is not the case of PA1015C2, for which η is lower than η^* because of the difference in orientation state of clay platelets during these shearing conditions. The first normal stress differences, N_1, of PA1015C2 is larger than that of PA1015B, showing the effect of the presence of clay on N_1. The model can predict well the viscosity of the neat polymer and its PNC, however the values of N_1 is overestimated by the model.

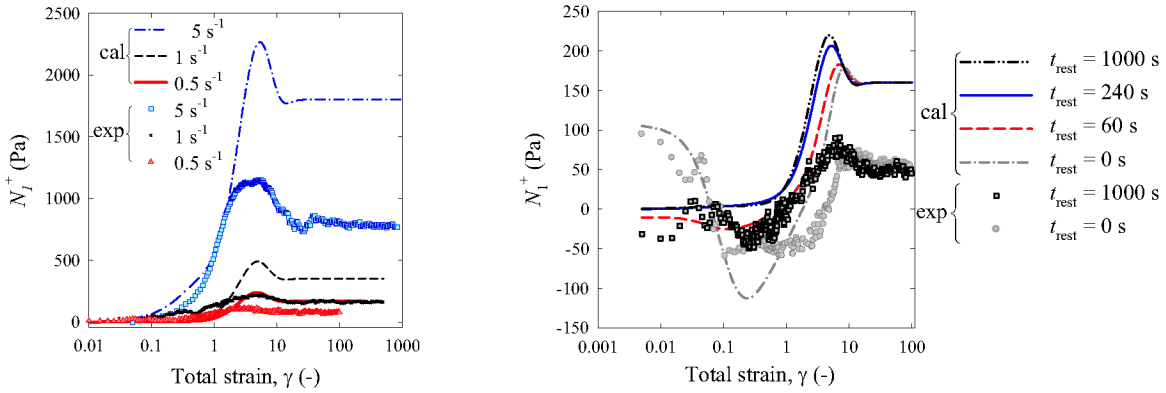
The stress growth viscosity, η^+, of PA1015B increases quite suddenly to the steady value of the plateau, suggesting the nearly Newtonian behavior of the PA-6. In the case of PA1015C2, the stress growth viscosity shows an overshoot before reaching the steady state plateau. The amplitude of the viscosity overshoot and the value of plateau are well predicted by the model. The viscosity overshoot is a well-known transient behavior of large aspect ratio particle filled systems, related to the orientation of particles in the flow direction. The N_1^+ of PA1015C2 shows also the same behavior with an overshoot at a strain later than that of viscosity (see Fig. 2a), qualitatively well described by the model. The immediate subsequent η^+ (t_{rest} = 0 s) of PA1015C2 in the opposite flow direction of the first test shows an overshoot. This reverse viscosity overshoot is due to reorientation of particles in the opposite

direction. The intensity of the viscosity overshoot increases with the delay time between the two consecutive tests suggesting the destruction of flow-induced oriented structure with the rest time. N_1^+, in reverse flow, decreases from the steady state plateau to negative values before an increase to the steady state, also qualitatively well-described by the model (Fig. 2b).



(a) (b)

FIGURE 1. Comparison of experimental results with model predictions for PA1015B and PA1015C2. (a) Steady shear and complex viscosity. (b) Steady first normal stress difference.



(a) (b)

FIGURE 2. Comparison of experimental results and model predictions of normal stress difference of PA1015C2 for (a) stress growth forward tests at 3 different shear rates of 0.5, 1 and 5 s^{-1}; (b) second consecutive shearing in reverse flow after different time delay ($\dot{\gamma}$ = 0.5 s^{-1}).

CONCLUSIONS

The transient behavior of polymer nanocomposites can reveal important information about the micro- and nano-structure of these materials. The steady and transient viscosity of PA and PA-PNC were well predicted by the model. However, the steady and transient first normal stress differences of PA-PNC were qualitatively well predicted but overestimated.

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